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## (54) CATALYST FOR PURIFYING EXHAUST GAS AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To increase NOX purification performance in the lean atmosphere by incorporating at least one kind of noble metal selected from among platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria.
CONSTITUTION: A catalyst for purifying HC, CO and NOX contained in exhaust gas discharged from an internal combustion engine, especially the catalyst A in which purification performance of NOX is excellent in the oxygen excess atmosphere is formed by incorporating at least one kind of noble metal selected from a group consisting of platinum, rhodium and palladium, and ceria, barium and potassium on a refactory inorganic carrier and carrying a part or the whole of the noble metal on the ceria. In order to furthermore increase the NOX absorption action of the catalyst for purifying exhaust gas, at least two pieces of catalyst are provided in the exhaust gas current of the engine. The catalyst containing zeolite carrying copper is arranged on the upstream side for the exhaust gas current and the catalyst A is arranged on the downstream side therefor.

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CLAIMS

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[Claim(s)]
[Claim 1] The catalyst for exhaust gas purification characterized by some or all of the noble metals concerned being supported by Seria including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least.
[Claim 2] The catalyst for exhaust-gas purification characterized by to consist of the catalyst bed B in which some or all of the noble metals concerned does not contain a potassium including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least, including a kind of noble metals chosen from the group which consists of the catalyst bed A currently supported by Seria, platinum, a rhodium, and palladium.
[Claim 3] The catalyst for exhaust gas purification characterized by establishing at least two catalysts into an engine exhaust air air current, arranging a copper support zeolite content catalyst to the upstream to an exhaust air air current, and arranging a catalyst according to claim 1 or 2 to the downstream.
[Claim 4] claims 1-3 -- the catalyst for exhaust gas purification to which Seria is characterized by being zirconium dissolution mold Seria in the catalyst for exhaust gas purification given [ one of ] in a term.
[Claim 5] claims 1-4 -- the catalyst for exhaust gas purification to which the content of a potassium and barium is converted into oxide weight, and per [ catalyst 1L ] and an each potassium are characterized by 0.1-20g, and barium being 0.1-100g in the catalyst for exhaust gas purification given [ one of ] in a term.
[Claim 6] The manufacture approach of the catalyst for exhaust gas purification characterized by calcinating after carrying out the coat of the alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, and the Seria powder which supported some or all of the noble metals concerned to catalyst support, and calcinating after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this.
[Claim 7] The manufacture approach of the catalyst for exhaust gas purification which is characterized by making burning temperature into 300-600 degrees C in manufacturing the catalyst for exhaust gas purification according to claim 6.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the catalyst for exhaust gas purification which is especially excellent in the purification engine performance of NOx under a hyperoxia ambient atmosphere, and its manufacture approach about the catalyst for exhaust gas purification which purifies the hydrocarbon (HC), the carbon monoxide (CO), and nitrogen oxides (NOx) in the exhaust gas discharged by internal combustion engines, such as a gasoline and a Diesel motorcar, and a boiler, and its manufacture approach.
[0002]
[Description of the Prior Art] In recent years, from **** of the exhaustion problem of petroleum resources, and a global warming issue, implementation of a low-fuel-consumption automobile is expected and development of a lean combustion automobile is desired especially to the gasoline automobile. In a lean combustion automobile, the exhaust gas ambient atmosphere at the time of lean combustion transit turns into a hyperoxia ambient atmosphere ("lean atmosphere" is called hereafter) compared with a theoretical **** condition (a "SUTOIKI condition" is called hereafter). In lean atmosphere, when the conventional three way component catalyst was fitted, there was a problem that an NOx cleaning effect became inadequate from the effect of superfluous oxygen. For this reason, development of the catalyst which can purify NOx under a hyperoxia ambient atmosphere was desired.
[0003] Before, it is proposed, and various catalysts which raise the NOx purification engine performance under lean atmosphere are divided roughly, and there are two kinds. One uses HC in exhaust gas as a reducing agent, and it oxidizes and NOx is purified, and another absorbs NOx under lean atmosphere and carries out emission purification of NOx under a SUTOIKI condition or an overfuel (rich) ambient atmosphere.
[0004] As a former typical thing, the catalyst which made JP,63-100919,A support copper (Cu) to a zeolite is indicated, for example.
[0005] On the other hand, as a latter typical thing, JP,5-168860,A is made to support a lanthanum etc. to platinum (Pt), and the catalyst using a lanthanum as an NOx absorber is indicated, for example.
[0006] However, the catalyst indicated by above-mentioned JP,5-168860,A has the problem that NOx absorptance is inadequate, and the catalyst for exhaust gas purification which is the purpose which solves this problem, for example, uses alkali and alkaline earth metal for JP,5-261287,A, JP,5-317652,A, and JP,6-31139,A is indicated. Moreover, the catalyst for exhaust gas purification containing alkali metal, alkaline earth metal, a rare earth metal, and an iron-group metal is indicated by JP,6-142458,A.
[0007]
[Problem(s) to be Solved by the Invention] However, the above-mentioned conventional exhaust gas purification catalyst has the inadequate NOx absorptivity ability under lean atmosphere, and is especially insufficient of the NOx absorptivity ability after durability.
[0008] Moreover, although the function as a three way component catalyst is also required of coincidence since NOx absorbed by lean atmosphere must be purified in SUTOIKI or a rich condition in the catalyst of such an NOx absorption mold If the alkali of a considerable amount and alkaline earth metal are added in order to obtain sufficient NOx absorption function, as mentioned above The strong basicity of alkali and alkaline earth metal affected the catalyst engine performance, the oxidation capacity of noble metals was reduced, and there was a problem that HC as a three way component catalyst and the inversion engine performance of CO became inadequate.
[0009] Therefore, the purpose of this invention is to offer the catalyst for exhaust gas purification which the NOx purification engine performance under the lean atmosphere which did not show activity sufficient with

the conventional catalyst can be raised, and can fully discover the function as a three way component catalyst, and its manufacture approach.

[0010]

[Means for Solving the Problem] this invention persons reached [ raising the NOx absorbing power under lean atmosphere, and ] a header and this invention by including at least a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium, Seria, and barium and a potassium, as a result of inquiring in order to solve the above-mentioned technical problem.

[0011] The catalyst for exhaust gas purification according to claim 1 is characterized by some or all of the noble metals concerned being supported by Seria including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, Seria, and barium and a potassium at least.

[0012] In order to raise HC and CO activity of said catalyst further, moreover, the catalyst for exhaust gas purification according to claim 2 At least a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium on fireproof inorganic support, The catalyst bed A with which some or all of the noble metals concerned is supported by Seria including Seria, and barium and a potassium It is characterized by consisting of the catalyst bed B which does not contain a potassium at least, including a kind of noble metals chosen from the group which consists of platinum, a rhodium, and palladium.

[0013] Furthermore, in order to raise further the NOx absorption of the catalyst for exhaust gas purification according to claim 1 or 2, the catalyst for exhaust gas purification according to claim 3 is characterized by establishing at least two catalysts into an engine exhaust air air current, arranging a copper support zeolite content catalyst to the upstream to an exhaust air air current, and arranging a catalyst according to claim 1 or 2 to the downstream.

[0014] in order [ furthermore, ] to raise further the NOx absorption and endurance of the catalyst for exhaust gas purification according to claim 1 to 3 -- the catalyst for exhaust gas purification according to claim 4 -- claims 1-3 -- in the catalyst for exhaust gas purification given [ one of ] in a term, Seria is characterized by being zirconium dissolution mold Seria.

[0015] in order [ furthermore, ] to raise the NOx absorptivity ability of the catalyst for exhaust gas purification according to claim 1 to 4 -- the catalyst for exhaust gas purification according to claim 5 -- claims 1-4 -- in the catalyst for exhaust gas purification given [ one of ] in a term, the content of a potassium and barium is converted into oxide weight, and per [ catalyst 1L ] and an each potassium are characterized by 0.1-20g, and barium being 0.1-100g.

[0016] At least one sort chosen from the group which consists of platinum, a rhodium, and palladium as noble metals used for the catalyst for exhaust gas purification of this invention is used. The content of said noble metals in a catalyst will not be limited especially if NOx absorbing power and the three way component catalyst engine performance at the time of SUTOIKI are fully obtained, but if fewer than 0.1g, even if the engine performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10g, as for the significant improvement in a property, per [ catalyst 1L / 0.1-10g ] are desirable from the point of not seeing.

[0017] The base material for supporting some or all of said noble metals has the point of promotion of NOx oxidation reaction required for NOx absorption to desirable Seria. As noble-metals support base materials other than Seria, in order to secure the dispersibility of noble metals, especially the dispersibility of the noble metals after durability, a heat-resistant inorganic material with a large specific surface area is suitable, and especially an activated alumina is desirable. In order to raise a heat-resistant specific surface area, the activated alumina which added rare earth elements, a zirconia, etc. may be used. When the dispersibility of sufficient noble metals will not be acquired if there is less amount of the activated alumina used than per [ catalyst 1L ] and 50g, but it is mostly used from 300g, it is desirable that they are 50-300g from the point that degradation is seen.

[0018] Moreover, Seria used for the catalyst for exhaust gas purification of this invention has especially desirable zirconium dissolution mold Seria from the point which raises NOx oxidizing quality ability and endurance. As for "dissolution", some cerium atoms in Seria say the thing in the condition of having permuted by the zirconium, and the oxide of such a condition is also called a multiple oxide here. As for this zirconium dissolution mold Seria, it is desirable that a part or all of the component has compound-ized.

[0019] As for the amount of the Seria concerned, it is desirable that they are per [ catalyst 1L / 10-100g ]. If it is less than 10g, even if the engine performance or the NOx oxidation ability of 3 yuan will not fully be obtained but it will exceed 100g conversely, the capable increase-in-quantity effectiveness is not acquired. Moreover, although the zirconium of zirconium dissolution mold Seria and especially the ratio of a cerium

are not limited, it is desirable that mol % of a zirconium is 5 - 50%. When mol % of a zirconium becomes except said range, NOx oxidation reaction required for NOx absorption or thermal resistance will fall.
[0020] According to the structure where some or all of said noble metals is supported by Seria, NOx oxidation reaction required for NOx absorption increases further, and obtains the outstanding NOx absorption.
[0021] Moreover, convert into metallic-oxide weight the content of the potassium used for the catalyst for exhaust gas purification of this invention, and barium, it catalyst 1L Hits, and it is desirable that a potassium is [ 0.1-20g, and barium ] 0.1-100g respectively. Even if NOx absorbing power is not fully acquired and it applies many amounts from this in case of an amount smaller than this, the capable increase-in-quantity effectiveness is not acquired.
[0022] Although the catalyst for exhaust gas purification according to claim 2 changes especially combining a catalyst bed A and the noble-metals catalyst bed B according to claim 1, arrangement of said A horizon and a B horizon is not limited especially from this thing [ that the effectiveness of layer separation is accepted in the case of which ], even if a B horizon is located in an A horizon lower layer at the upper layer, and even if reverse.
[0023] At least one sort of noble metals chosen from the group which consists of platinum, a rhodium, and palladium are contained in the noble metals in said noble-metals catalyst bed B. Moreover, if fewer than 0.1g, even if the engine performance of 3 sufficient yuan will not be obtained but it will use it mostly from 10g, as for the significant improvement in the engine performance, per [ catalyst 1L / 0.1-10g ] are desirable [ the content of the noble metals will not be limited especially if NOx absorbing power and the three way component catalyst engine performance at the time of SUTOIKI are fully obtained, but ] from the point of not seeing. Moreover, a potassium must not be contained in the catalyst bed B concerned, and this is for not reducing the oxidation engine performance to HC and CO of noble metals, and maintaining highly.
[0024] In order to secure the dispersibility of noble metals, especially the dispersibility of the noble metals after durability to the base material for supporting the noble metals in the catalyst bed B concerned, a heat-resistant inorganic material with a large specific surface area is suitable, and especially an activated alumina is desirable. In order to raise a heat-resistant specific surface area, the activated alumina which added rare earth elements, a zirconia, etc. may be used. If there is less amount of the activated alumina used than per [ catalyst 1L ] and 50g, even if the engine performance will fall without acquiring the dispersibility of sufficient noble metals and it will use mostly from 300g, it is desirable that they are 50-300g from the point that degradation is seen.
[0025] Moreover, if fewer than 100g, even if sufficient NOx reducibility ability will not be obtained but it will use it mostly from 300g, as for the significant improvement in the engine performance, per [ catalyst support 1L / 100-300g ] are desirable [ especially if the content of Cu support zeolite catalyst prepared in the upstream to the exhaust gas style in invention according to claim 3 is an amount which shows an NOx cleaning effect, it will not be limited, but ] from the point of not seeing. In order to raise catalytic activity and endurance, Co, calcium, P, Ce, Nd, etc. may be added. That the activity after Cu ion exchange excels [ that ] in thermal resistance highly as a zeolite is used preferably, for example, there are a PENTARU mold zeolite, Y mold zeolite, mordenite, a ferrierite, etc.
[0026] The installation approach to the exhaust air system of the Cu support zeolite catalyst concerned and a catalyst according to claim 1 or 2 It is important to install a catalyst according to claim 1 or 2 in the upstream for Cu support zeolite catalyst to an exhaust gas style again at the downstream to an exhaust gas style. For example, the approach that the approach of equipping with and arranging two sorts of catalysts in one catalytic converter, the method of putting said two sorts of catalysts into a separate converter, and installing them, etc. are well-known can be used. Especially the installation location of a catalyst is not limited, for example, a manifold directly under location, an under floor location, etc. are raised. With the catalyst per the preceding paragraph of this catalyst system, and each latter part, when the purification engine performance is not enough, both the preceding paragraph, and both [ either or ] may be further made [ two or more ], or a variety catalyst may be added.
[0027] Honeycomb support, metal support, etc. which have the monolith structure which can use it, choosing suitably from well-known catalyst support as catalyst support used by this invention for example, which consists of a fireproof ingredient are mentioned. As for especially the configuration of this catalyst support, it is desirable to usually use it in a honeycomb configuration, although not restricted, it is possible also for using the honeycomb which consists of metallic materials, such as ferrite system stainless steel, although many things of quality of cordierite, such as a ceramic, are generally used as this honeycomb material, and may fabricate the catalyst powder itself in a honeycomb configuration further. By making the

configuration of a catalyst into the shape of a honeycomb, since the catalyst area of a catalyst and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for automobiles etc., it is very advantageous.

[0028] In order to manufacture the catalyst for exhaust gas purification of this invention For example, prepare the compound of the element to support beforehand and the coat of the water-soluble slurry which ground such mixture with wet is carried out to monolith support. After drying, the coat of the components other than a potassium and barium is carried out to monolith support among the approach of calcinating and acquiring, and the element to support, after drying, it calcinates, and there is a method of sinking in and acquiring the water solubility which subsequently contains the salt of each component of a potassium and barium.

[0029] Especially the manufacture approach of the catalyst for exhaust gas purification according to claim 6 The alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, It is characterized by calcinating, after carrying out the coat of the Seria powder which supported some or all of the noble metals concerned to catalyst support, and calcinating, after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this.

[0030] Moreover, in manufacturing the catalyst for exhaust gas purification according to claim 6, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 is characterized by making burning temperature into 300-600 degrees C.

[0031] Although it can be used as a raw material compound for catalyst preparation combining a nitrate, a carbonate, ammonium salt, acetate, a halogenide, an oxide, etc., it is desirable to use a water-soluble salt especially from a viewpoint which raises the catalyst engine performance to HC and NOx. Unless it is not limited to an approach special as the method of preparation but is accompanied by the remarkable maldistribution of a component, various approaches, such as a well-known evaporation-to-dryness method, settling, and the sinking-in method, can be used.

[0032] There are an approach of calcinating and acquiring, after drying a cerium and the mixed water solution containing the salt of a zirconium, for example, although especially the manufacture approach especially of zirconium dissolution mold Seria is not limited, and the approach of calcinating, after drying the precipitate which added and obtained ammonium, the ammonium carbonate, and the citric acid in the mixed water solution of each salt.

[0033] Moreover, the above-mentioned heat treatment is performed under air or air circulation, and if 300 degrees C - 600 degrees C are desirable and is less than 300 degrees C, the whole will not serve as an oxide, but if it exceeds 600 degrees C, specific surface area will fall, and the burning temperature is not desirable.

[0034]

[Function] The catalyst for exhaust gas purification according to claim 1 contains at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium, Seria, and barium and a potassium, and when some or all of said noble metals is supported by Seria and both live together, it raises NOx oxidation reaction required for NOx absorption. Moreover, the NOx absorptance which barium and a potassium originally have is to be fully able to demonstrate because barium and a potassium touch the interface of noble metals and Seria. After durability makes it hard for these factors to lap, and to raise NOx absorbing power, and to fall the catalyst engine performance.

[0035] Especially the catalyst for exhaust gas purification according to claim 2 obtains sufficient three way component catalyst engine performance, obtaining NOx absorptivity ability by considering as the two-layer structure which comes to combine the catalyst bed A and the above-mentioned noble-metals support catalyst bed B containing the above-mentioned noble metals, Seria, and barium and a potassium. The noble metals in a catalyst bed A show the operation which mainly promotes absorption of NOx as described above. On the other hand, the noble metals in a catalyst bed B promote oxidation of HC and CO further, and raise the reduction effectiveness of NOx. Therefore, if a potassium is contained in a catalyst B horizon, in order that a potassium may reduce HC and CO oxidation engine performance of said noble metals, don't contain a potassium in the catalyst bed B concerned.

[0036] It is especially related with the catalyst for exhaust gas purification according to claim 3. Moreover, conventionally NOx purification catalysts, such as Cu support zeolite catalyst, and NOx absorption catalysts, such as Pt-lanthanum catalyst, for example, on the property, If the HC/NOx ratio in exhaust gas is small, a cleaning effect will not fully be acquired, and if Lean performs stationary transit in the latter, an NOx absorbed amount will reach saturation, and the former has the problem that absorption is lost soon, and was not able to purify NOx under the broad service condition. Therefore, invention according to claim 3 is

raising the absorption of a latter NOx absorption catalyst by once contacting exhaust gas to Cu support zeolite catalyst. The absorption is oxidation of NOx required for NOx absorption at for example, Cu support zeolite catalyst having advanced promptly, and having assisted work of an NOx absorber, and HC, NOx and O2 with Cu support zeolite catalyst convenient to NOx absorption. It is possible that it has changed into concentration etc.
[0037] Furthermore, compared with the case where Seria purer than Seria is zirconium dissolution mold Seria is used, the NOx oxidation engine performance and endurance increase, and especially the catalyst for exhaust gas purification according to claim 4 acquires the outstanding NOx absorption and endurance.
[0038] Furthermore, especially the catalyst for exhaust gas purification according to claim 5 obtains NOx absorptivity ability by limiting, as the content of a potassium and barium was respectively described above, securing the engine performance at the time of SUTOIKI.
[0039] Moreover, the manufacture approach of the catalyst for exhaust gas purification according to claim 6 The alumina powder which supported at least a kind of noble metals chosen from the group which consists of platinum, palladium, and a rhodium on fireproof inorganic support, By considering as the process which calcinates after carrying out the coat of the Seria powder which supported some or all of the noble metals concerned to catalyst support, and is calcinated after, sinking in the mixed water solution of the metal salt of a potassium and barium subsequently to this A potassium and barium will touch the interface of noble metals and Seria, and the NOx absorptance which barium and a potassium originally have can fully be demonstrated.
[0040] Moreover, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 brings about the uniform dispersibility of noble metals into a catalyst, without spoiling the dispersibility of noble metals by limiting with 300-600 degrees C, as heat treatment burning temperature was described above.
[0041]
[Example] A following example and the following example of a comparison explain this invention.
The nitric-acid rhodium (Rh) water solution was sunk into example 1 activated-alumina powder, it calcinated at 400 degrees C after desiccation for 1 hour, and Rh support activated-alumina powder (powder A) was obtained. Rh concentration of this powder A was 2.0 % of the weight. After sinking in and drying a dinitro diamine platinum (Pt) water solution to activated-alumina powder, it calcinated at 400 degrees C for 1 hour, and Pt support activated-alumina powder (powder B) was obtained. Pt concentration of this powder B was 4.0 % of the weight. The 108g (powder A) of the above-mentioned Rh support activated-alumina powder, 531g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 81g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. Into the ingredient of the coat layer weight 100 g/L-support concerned, the mixed water solution of potassium acetate and barium acetate was calcinated at 400 degrees C for 1 hour, after sinking in and drying, and the catalyst for exhaust gas purification was acquired into it. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.
[0042] The catalyst for exhaust gas purification was acquired like the example 1 except having converted the content of example 2 potassium and barium into the oxide respectively, and having made it into 10 g/L and 40 g/L.
[0043] Ammonia was added in the mixed water solution of example 3 zirconium nitrate and a cerium nitrate, obtained sediment was filtered, after drying, it calcinated at 400 degrees C for 3 hours, and zirconium dissolution mold Seria powder (powder C) was obtained. The amount of the zirconium contained in the zirconium dissolution mold Seria powder C concerned was converted into a metal mol, and were Zr/Ce=5/95. The catalyst for exhaust gas purification was acquired like the example 1 except having used this zirconium dissolution mold Seria powder C instead of the activity Seria powder of an example 1.
[0044] The zirconium dissolution mold Seria powder (powder D) of example 4 Zr/Ce=40/60 was obtained by the same approach as an example 3, and the catalyst for exhaust gas purification was acquired like the example 1 except having used this zirconium dissolution mold Seria powder D instead of the activity Seria powder of an example 1.
[0045] After sinking in and drying a dinitrodiammine platinum (Pt) water solution to example 5 activity Seria powder, it calcinated at 400 degrees C for 1 hour, and Pt support activity Seria powder (powder E) was

obtained. Pt concentration of this powder E was 2.0 % of the weight. 108g (powder A) of Rh support activated-alumina powder obtained in the example 1, 351g (powder B) of Pt support activated-alumina powder, the 180g (powder E) of the above-mentioned Pt support activity Seria powder, 261g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0046] The catalyst for exhaust gas purification was acquired like the example 5 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 3 instead of the activity Seria powder of example 6 example 5.

[0047] 72g (powder A) of Rh support activated-alumina powder obtained in the example 7 example 1, 348g (powder B) of Pt support activated-alumina powder, 120g of activity Seria powder, 60g of activated-alumina powder, 124g of potassium acetate, 428g of barium acetate, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the lower layer catalyst of coat layer weight 75 g/L-support was acquired. The content of the potassium in the ingredient concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L. 108g (powder A) of Rh support activated-alumina powder obtained in the example 1, 540g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 72g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the above-mentioned 75 g/L-support, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and combining the upper catalyst and the lower layer catalyst, it was total and the catalyst for exhaust gas purification of coat layer weight 125 g/L-support was acquired.

[0048] The catalyst for exhaust gas purification was acquired like the example 7 except making reverse the upper and lower sides of a coat layer by making a lower layer catalyst into the upper catalyst, using the upper catalyst in example 8 example 7 as a lower layer catalyst.

[0049] 108g (powder A) of Rh support activated-alumina powder obtained in the example of comparison 1 example 1, 531g (powder B) of Pt support activated-alumina powder, 261g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.

[0050] 108g (powder A) of Rh support activated-alumina powder obtained in the example of comparison 2 example 1, 531g (powder B) of Pt support activated-alumina powder, 180g of activity Seria powder, 81g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification of coat layer weight 100 g/L-support was acquired.

[0051] After sinking in and drying a dinitrodiammine palladium water solution to example 9 activated-alumina powder, it calcinated at 400 degrees C for 1 hour, and Pd support activated-alumina powder (powder F) was obtained. Pd concentration of this powder F was 4.0 % of the weight. The 630g (powder F) of the Pd support activated-alumina powder concerned, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the

nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.
[0052] The catalyst for exhaust gas purification was acquired like the example 9 except having converted the content of example 10 potassium and barium into the oxide respectively, and having made it into 10 g/L and 40 g/L.
[0053] The catalyst for exhaust gas purification was acquired like the example 9 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 11 example 3 instead of the activity Seria powder of an example 9.
[0054] The catalyst for exhaust gas purification was acquired like the example 9 except having used the zirconium dissolution mold Seria powder (powder D) obtained in the example 12 example 4 instead of the activity Seria powder of an example 9.
[0055] After sinking in and drying a dinitrodiammine palladium water solution to example 13 activity Seria powder, it calcinated at 400 degrees C for 1 hour, and Pd support activity Seria powder (powder G) was obtained. Pd concentration of this powder G was 4.0 % of the weight. 450g (powder F) of Pd support activated-alumina powder obtained in the example 9, the 180g (powder G) of the above-mentioned Pd support activity Seria powder, 270g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst 15 concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.
[0056] The catalyst for exhaust gas purification was acquired like the example 13 except having used the zirconium dissolution mold Seria powder (powder C) obtained in the example 14 example 3 instead of the activity Seria powder of an example 13.
[0057] 420g (powder F) of Pd support activated-alumina powder obtained in the example 15 example 9, 120g of activity Seria powder, 60g of activated-alumina powder, 124g of potassium acetate, 428g of barium acetate, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the lower layer catalyst of coat layer weight 75 g/L-support was acquired. The content of the potassium in the ingredient concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L. 630g (powder F) of Pd support activated-alumina powder obtained in the example 9, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the above-mentioned 75 g/L-support, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and combining the upper catalyst and the lower layer catalyst, it was total and the catalyst for exhaust gas purification of 125 g/L-support was acquired.
[0058] The catalyst for exhaust gas purification was acquired like the example 15 except making reverse the upper and lower sides of a coat layer by making a lower layer catalyst into the upper catalyst, using the upper catalyst in example 16 example 15 as a lower layer catalyst.
[0059] Preferential grinding of 630g (powder F) of Pd support activated-alumina powder obtained in the example of comparison 3 example 9, 270g of activated-alumina powder, and the 900g of the water was added, thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the ingredient of coat layer weight 100 g/L-support was obtained. After sinking in and drying the mixed water solution of potassium acetate and barium acetate into the ingredient of the 100 g/L-support

concerned, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification was acquired. The content of the potassium in the catalyst concerned and barium was respectively converted into the oxide, and were 5 g/L, and 20g/L.
[0060] 630g (powder F) of Pd support activated-alumina powder obtained in the example of comparison 4 example 9, 180g of activity Seria powder, 90g of activated-alumina powder, and 900g of water were added, it supplied to the magnetic ball mill, preferential grinding was carried out to it, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst for exhaust gas purification of coat layer weight 100 g/L-support was acquired.
[0061] After repeating the activity filtered after mixing and stirring 5.2kg of copper-nitrate water solutions and 2kg of zeolite powder of 170.2 mols of examples, and L 3 times, it dried and calcinated and Cu support zeolite powder (powder H) was obtained. Cu concentration of this powder H was 5%. Preferential grinding of 810g [ of this Cu support zeolite powder ] (powder H) and silica sol (20% of solid content) 450g and the 540g of the water was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained. After having made this slurry liquid adhere to the nature monolith support of cordierite (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and Cu support zeolite catalyst of coat layer weight 300 g/L-support was acquired. The catalyst acquired in the example 1 in this Cu support zeolite catalyst by the upstream of exhaust air flow again has been arranged to the downstream.
[0062] The catalyst acquired in the example 2 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 18 example 17 has been arranged to the downstream.
[0063] The catalyst acquired in the example 3 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 19 example 17 has been arranged to the downstream.
[0064] The catalyst acquired in the example 4 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 20 example 17 has been arranged to the downstream.
[0065] The catalyst acquired in the example 5 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 21 example 17 has been arranged to the downstream.
[0066] The catalyst acquired in the example 6 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 22 example 17 has been arranged to the downstream.
[0067] The catalyst acquired in the example 7 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 23 example 17 has been arranged to the downstream.
[0068] The catalyst acquired in the example 8 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 24 example 17 has been arranged to the downstream.
[0069] The catalyst acquired in the example 9 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 25 example 17 has been arranged to the downstream.
[0070] The catalyst acquired in the example 10 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 26 example 17 has been arranged to the downstream.
[0071] The catalyst acquired in the example 11 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 27 example 17 has been arranged to the downstream.
[0072] The catalyst acquired in the example 12 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 28 example 17 has been arranged to the downstream.
[0073] The catalyst acquired in the example 13 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 29 example 17 has been arranged to the downstream.
[0074] The catalyst acquired in the example 14 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 30 example 17 has been arranged to the downstream.
[0075] The catalyst acquired in the example 15 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 31 example 17 has been arranged to the downstream.
[0076] The catalyst acquired in the example 16 by the upstream of exhaust air flow again in Cu support zeolite catalyst acquired in the example 32 example 17 has been arranged to the downstream.
[0077] The catalyst presentation of the above-mentioned examples 1-32 and the examples 1-4 of a comparison is shown in the next tables 1 and 2.
[Table 1]

| | 貴金属（g/L） | | | 添加材（酸化物g/L） | | |
|---|---|---|---|---|---|---|
| | Pt | Rh | Pd | Ce | K | Ba |
| 実施例1 / 実施例17 | 1.18 | 0.24 | − | 20.0 | 5.0 | 20.0 |
| 実施例2 / 実施例18 | 1.18 | 0.24 | − | 20.0 | 10.0 | 40.0 |
| 実施例3 / 実施例19 | 1.18 | 0.24 | − | 20.0 (*1) | 5.0 | 20.0 |
| 実施例4 / 実施例20 | 1.18 | 0.24 | − | 20.0 (*2) | 5.0 | 20.0 |
| 実施例5 / 実施例21 | 1.18 | 0.24 | − | 20.0 | 5.0 | 20.0 |
| 実施例6 / 実施例22 | 1.18 | 0.24 | − | 20.0 | 5.0 | 20.0 |
| 実施例7 / 実施例23 | 1.18 | 0.24 | − | 20.0 | 5.0 | 20.0 |
| 実施例8 / 実施例24 | 1.18 | 0.24 | − | 20.0 | 5.0 | 20.0 |
| 実施例9 / 実施例25 | − | − | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例10 / 実施例26 | − | − | 2.83 | 20.0 | 10.0 | 40.0 |
| 実施例11 / 実施例27 | − | − | 2.83 | 20.0 (*1) | 5.0 | 20.0 |
| 実施例12 / 実施例28 | − | − | 2.83 | 20.0 (*2) | 5.0 | 20.0 |
| 実施例13 / 実施例29 | − | − | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例14 / 実施例30 | − | − | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例15 / 実施例31 | − | − | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例16 / 実施例32 | − | − | 2.83 | 20.0 | 5.0 | 20.0 |

(*1)：Zr／Ceモル比＝5／95
(*2)：Zr／Ceモル比＝40／60

[Table 2]

| | 貴金属（g/L） | | | 添加材（g/L） | | |
|---|---|---|---|---|---|---|
| | Pt | Rh | Pd | Ce | K | Ba |
| 比較例1 | 1.18 | 0.24 | − | − | 5.0 | 20.0 |
| 比較例2 | 1.18 | 0.24 | − | 20.0 | − | − |
| 比較例3 | − | − | 2.83 | − | 10.0 | 10.0 |
| 比較例4 | − | − | 2.83 | 20.0 | − | − |

[0078] About the catalyst and catalyst system of the example of trial 1 aforementioned examples 1-32, and the examples 1-4 of a comparison, catalytic activity evaluation after the first stage and durability was performed on condition that the following. The automatic evaluation equipment using the model gas which imitated the exhaust gas of an automobile was used for activity evaluation.
[0079] The durable condition engine 4400cc exhaust air system was equipped with the catalyst, at 600 degrees C, it operated for 50 hours and durability was performed.
[0080] Evaluation condition catalytic activity evaluation equips the exhaust air system of an engine with a displacement of 2000 cc with each catalyst. Operation for 30 seconds for 30 seconds by A/F=14.6 (SUTOIKI condition) after that A/F=22 (lean atmosphere) 1 cycle deed, The average invert ratio was measured respectively, the average invert ratio in this A/F=14.6 (SUTOIKI condition) and the average invert ratio in A/F=22 (lean atmosphere) were averaged, and it considered as the total invert ratio. This evaluation

was respectively performed after the first stage and durability, and the following formulas determined the catalytic activity evaluation value.
[Equation 1]

$$\mathrm{NOx}転化率(\%) = \frac{〔触媒層入口\mathrm{NOx}濃度〕 - 〔触媒層出口\mathrm{NOx}濃度〕}{〔触媒層入口\mathrm{NOx}濃度〕} \times 100$$

（ＨＣ，ＣＯも同様）

[0081] The catalytic activity evaluation result obtained as a total invert ratio is shown in Tables 3-5. Compared with the example of a comparison, catalytic activity of the example was high and it was able to check the effectiveness of this invention mentioned later.
[Table 3]

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | ＨＣ | ＣＯ | ＮＯｘ | ＨＣ | ＣＯ | ＮＯｘ |
| 実施例 1 | 91 | 100 | 90 | 92 | 97 | 62 |
| 実施例 2 | 88 | 99 | 93 | 91 | 97 | 65 |
| 実施例 3 | 93 | 100 | 92 | 95 | 99 | 67 |
| 実施例 4 | 93 | 100 | 92 | 96 | 99 | 66 |
| 実施例 5 | 92 | 100 | 92 | 93 | 97 | 64 |
| 実施例 6 | 96 | 100 | 95 | 95 | 99 | 68 |
| 実施例 7 | 92 | 100 | 91 | 93 | 98 | 63 |
| 実施例 8 | 91 | 100 | 91 | 93 | 98 | 63 |
| 比較例 1 | 88 | 100 | 87 | 89 | 95 | 59 |
| 比較例 2 | 90 | 100 | 89 | 90 | 96 | 50 |

[Table 4]

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | ＨＣ | ＣＯ | ＮＯｘ | ＨＣ | ＣＯ | ＮＯｘ |
| 実施例 9 | 95 | 100 | 93 | 96 | 99 | 65 |
| 実施例10 | 89 | 99 | 93 | 94 | 98 | 67 |
| 実施例11 | 93 | 100 | 95 | 95 | 99 | 68 |
| 実施例12 | 95 | 100 | 96 | 96 | 99 | 68 |
| 実施例13 | 95 | 100 | 96 | 95 | 97 | 65 |
| 実施例14 | 97 | 100 | 96 | 95 | 99 | 70 |
| 実施例15 | 94 | 100 | 93 | 94 | 98 | 65 |
| 実施例16 | 94 | 100 | 93 | 95 | 98 | 63 |
| 比較例 3 | 89 | 100 | 89 | 89 | 95 | 56 |
| 比較例 4 | 90 | 100 | 89 | 90 | 96 | 51 |

[Table 5]

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | HC | CO | NOx | HC | CO | NOx |
| 実施例17 | 92 | 100 | 98 | 92 | 98 | 77 |
| 実施例18 | 90 | 100 | 98 | 91 | 98 | 79 |
| 実施例19 | 93 | 100 | 96 | 95 | 99 | 78 |
| 実施例20 | 93 | 100 | 96 | 96 | 99 | 80 |
| 実施例21 | 92 | 100 | 97 | 93 | 97 | 82 |
| 実施例22 | 96 | 100 | 96 | 95 | 99 | 83 |
| 実施例23 | 92 | 100 | 98 | 93 | 98 | 79 |
| 実施例24 | 91 | 100 | 98 | 94 | 98 | 79 |
| 実施例25 | 96 | 100 | 97 | 90 | 95 | 79 |
| 実施例26 | 94 | 100 | 95 | 93 | 96 | 80 |
| 実施例27 | 95 | 100 | 96 | 96 | 99 | 80 |
| 実施例28 | 95 | 99 | 96 | 95 | 98 | 80 |
| 実施例29 | 96 | 100 | 98 | 96 | 99 | 83 |
| 実施例30 | 98 | 100 | 96 | 95 | 99 | 86 |
| 実施例31 | 95 | 100 | 96 | 95 | 98 | 80 |
| 実施例32 | 95 | 100 | 97 | 95 | 98 | 80 |

[0082]
[Effect of the Invention] When noble metals, Seria, and barium and a potassium are contained and some or all of noble metals is supported by Seria, the catalyst for exhaust gas purification according to claim 1 can raise the NOx purification engine performance under the lean atmosphere from which activity sufficient with the conventional catalyst is not acquired by raising NOx oxidation reaction required for NOx absorption, and can fully discover the function as a three way component catalyst after durability.
[0083] In addition to said effectiveness, the catalyst for exhaust gas purification according to claim 2 can raise HC and CO activity further by combining a noble-metals support layer and a catalyst bed according to claim 1 with arbitration up and down.
[0084] In addition to the above-mentioned effectiveness, the catalyst for exhaust gas purification according to claim 3 can raise NOx absorption further, when a copper support zeolite content catalyst is arranged to the upstream and it arranges a catalyst above-mentioned claim 1 or given in two to the downstream to an exhaust air air current.
[0085] In addition to the above-mentioned effectiveness, the catalyst for exhaust gas purification according to claim 4 can raise the NOx oxidation engine performance and endurance further by making Seria into zirconium dissolution mold Seria further.
[0086] When the catalyst for exhaust gas purification according to claim 5 specifies the content of a potassium and barium further, in addition to the above-mentioned effectiveness, the engine performance at the time of SUTOIKI will also be secured.
[0087] By passing through the process which gave [ above-mentioned ] explanation, a potassium and barium can fully touch the interface of noble metals and Seria, and the manufacture approach of the catalyst for exhaust gas purification according to claim 6 can manufacture the catalyst for exhaust gas purification according to claim 1 which can fully demonstrate NOx absorptance by this simple.
[0088] In addition to the above-mentioned effectiveness, the manufacture approach of the catalyst for exhaust gas purification according to claim 7 can make homogeneity further distribution of the noble metals to the inside of the catalyst for exhaust gas purification by limiting heat treatment burning temperature further.

[Translation done.]

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## (54) CATALYST FOR PURIFYING EXHAUST GAS AND ITS PRODUCTION

(57) Abstract:

PURPOSE: To increase NOX purification performance in the lean atmosphere by incorporating at least one kind of noble metal selected from among platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria.

CONSTITUTION: A catalyst for purifying HC, CO and NOX contained in exhaust gas discharged from an internal combustion engine, especially the catalyst A in which purification performance of NOX is excellent in the oxygen excess atmosphere is formed by incorporating at least one kind of noble metal selected from a group consisting of platinum, rhodium and palladium, and ceria, barium and potassium on a refractory inorganic carrier and carrying a part or the whole of the noble metal on the ceria. In order to furthermore increase the NOX absorption action of the catalyst for purifying exhaust gas, at least two pieces of catalyst are provided in the exhaust gas current of the engine. The catalyst containing zeolite carrying copper is arranged on the upstream side for the exhaust gas current and the catalyst A is arranged on the downstream side therefor.

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(54)【発明の名称】　排気ガス浄化用触媒及びその製造方法

(57)【要約】

【目的】　従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるＮＯｘ浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発現することができる排気ガス浄化用触媒及びその製造方法を提供する。

【構成】　耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持される。また、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層Ａと、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層Ｂとから成る。更にエンジン排気気流中に触媒を少なくとも２個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に上記２種のいずれか一方の触媒を配置する。

【特許請求の範囲】

【請求項１】　耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されていることを特徴とする排気ガス浄化用触媒。

【請求項２】　耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層Ａと、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層Ｂとから成ることを特徴とする排気ガス浄化用触媒。

【請求項３】　エンジン排気気流中に触媒を少なくとも２個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に請求項１又は２記載の触媒を配置することを特徴とする排気ガス浄化用触媒。

【請求項４】　請求項１～３いずれかの項記載の排気ガス浄化用触媒において、セリアが、ジルコニウム固溶型セリアであることを特徴とする排気ガス浄化用触媒。

【請求項５】　請求項１～４いずれかの項記載の排気ガス浄化用触媒において、カリウム及びバリウムの含有量は、酸化物重量に換算して、触媒１Ｌあたり、各々カリウムが０．１～２０ｇ、バリウムが０．１～１００ｇであることを特徴とする排気ガス浄化用触媒。

【請求項６】　耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成することを特徴とする排気ガス浄化用触媒の製造方法。

【請求項７】　請求項６記載の排気ガス浄化用触媒を製造するにあたり、焼成温度を３００～６００℃とすることを特徴とする排気ガス浄化用触媒の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、ガソリン及びディーゼル自動車、ボイラー等の内燃機関から排出される排気ガス中の炭化水素（ＨＣ）、一酸化炭素（ＣＯ）および窒素酸化物（ＮＯｘ）を浄化する排気ガス浄化用触媒及びその製造方法に関し、特に酸素過剰雰囲気下でのＮＯｘの浄化性能に優れる排気ガス浄化用触媒及びその製造方法に関する。

【０００２】

【従来の技術】近年、石油資源の枯渇問題および地球温暖化問題の関点から、低燃費自動車の実現が期待されており、特にガソリン自動車に対しては希薄燃焼自動車の開発が望まれている。希薄燃焼自動車においては、希薄燃焼走行時の排気ガス雰囲気は、理論空燃状態（以下、「ストイキ状態」と称す）に比べて酸素過剰雰囲気（以下、「リーン雰囲気」と称す）となる。リーン雰囲気において、従来の三元触媒を適応させた場合には、過剰な酸素の影響からＮＯｘ浄化作用が不十分となるという問題があった。このため酸素過剰雰囲気下においてもＮＯｘを浄化できる触媒の開発が望まれていた。

【０００３】従来より、リーン雰囲気下におけるＮＯｘ浄化性能を向上させる触媒は種々提案されており、大別して２種類ある。一つは排気ガス中のＨＣを還元剤としてＮＯｘを酸化して浄化するものであり、もう一つはリーン雰囲気下でＮＯｘを吸収し、ストイキ状態あるいは燃料過剰（リッチ）雰囲気下でＮＯｘを放出浄化するものである。

【０００４】前者の代表的なものとしては、例えば特開昭６３－１００９１９号公報に、銅（Ｃｕ）をゼオライトに担持させた触媒が開示されている。

【０００５】一方、後者の代表的なものとしては、例えば特開平５－１６８８６０号公報に、ランタン等を白金（Ｐｔ）に担持させてランタンをＮＯｘ吸収材として用いる触媒が開示されている。

【０００６】しかし上記特開平５－１６８８６０号公報に開示された触媒は、ＮＯｘ吸収能力が不十分であるという問題があり、かかる問題を解決する目的で、例えば特開平５－２６１２８７号公報、特開平５－３１７６５２号公報及び特開平６－３１１３９号公報にアルカリ、アルカリ土類金属を用いる排気ガス浄化用触媒が開示されている。また、特開平６－１４２４５８号公報には、アルカリ金属、アルカリ土類金属、希土類金属、鉄属金属を含有する排気ガス浄化用触媒が開示されている。

【０００７】

【発明が解決しようとする課題】しかしながら、上記従来の排気ガス浄化触媒は、リーン雰囲気下におけるＮＯｘ吸収性能が不十分であり、特に耐久後のＮＯｘ吸収性能が不足している。

【０００８】またこの様なＮＯｘ吸収型の触媒においては、リーン雰囲気で吸収したＮＯｘをストイキあるいはリッチ状態時に浄化しなければならないので、三元触媒としての機能も同時に要求されるが、上述したように十分なＮＯｘ吸収機能を得るために相当量のアルカリ、アルカリ土類金属を添加すると、アルカリ、アルカリ土類金属の強い塩基性が触媒性能に影響を及ぼして貴金属の酸化能力を低下させ、三元触媒としてのＨＣ，ＣＯの転化性能が不十分になるという問題があった。

【０００９】従って、本発明の目的は、従来の触媒では十分な活性を示さなかったリーン雰囲気下におけるＮＯｘ浄化性能を向上させることができ、かつ三元触媒としての機能を十分に発現することができる排気ガス浄化用触媒及びその製造方法を提供するにある。

【００１０】

【課題を解決するための手段】本発明者らは、上記課題を解決するために研究した結果、白金、ロジウム及びパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウムとカリウムとを含むことにより、リーン雰囲気下でのＮＯｘ吸収能を向上させることを見出し、本発明に到達した。

【００１１】請求項１記載の排気ガス浄化用触媒は、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されていることを特徴とする。

【００１２】また前記触媒のＨＣ及びＣＯ活性を更に向上させるために、請求項２記載の排気ガス浄化用触媒は、耐火性無機担体上に、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含み、当該貴金属の一部若しくは全部がセリアに担持されている触媒層Ａと、白金、ロジウムおよびパラジウムから成る群より選ばれた少なくとも一種の貴金属を含みかつカリウムを含有しない触媒層Ｂとから成ることを特徴とする。

【００１３】更に、請求項１又は２に記載の排気ガス浄化用触媒のＮＯｘ吸収作用を更に高めるために、請求項３記載の排気ガス浄化用触媒は、エンジン排気気流中に触媒を少なくとも２個設け、排気気流に対して上流側に銅担持ゼオライト含有触媒を配置し、下流側に請求項１又は２記載の触媒を配置することを特徴とする。

【００１４】更に、請求項１～３に記載の排気ガス浄化用触媒のＮＯｘ吸収作用及び耐久性を更に高めるために、請求項４記載の排気ガス浄化用触媒は、請求項１～３いずれかの項記載の排気ガス浄化用触媒において、セリアが、ジルコニウム固溶型セリアであることを特徴とする。

【００１５】更に、請求項１～４に記載の排気ガス浄化用触媒のＮＯｘ吸収性能を高めるために、請求項５記載の排気ガス浄化用触媒は、請求項１～４いずれかの項記載の排気ガス浄化用触媒において、カリウム及びバリウムの含有量は、酸化物重量に換算して、触媒１Ｌあたり、各々カリウムが０．１～２０ｇ、バリウムが０．１～１００ｇであることを特徴とする。

【００１６】本発明の排気ガス浄化用触媒に用いる貴金属としては、白金、ロジウムおよびパラジウムから成る群より選ばれる少なくとも１種が用いられる。触媒中の前記貴金属の含有量は、ＮＯｘ吸収能とストイキ時の三元触媒性能が十分に得られれば特に限定されないが、０．１ｇより少ないと十分な三元性能が得られず、１０ｇより多く使用しても有意な特性向上はみられない点から触媒１Ｌあたり０．１～１０ｇが好ましい。

【００１７】前記貴金属の一部又は全部を担持するための基材は、ＮＯｘ吸収に必要なＮＯｘ酸化反応の促進の点からセリアが好ましい。セリア以外の貴金属担持基材としては、貴金属の分散性、特に耐久後の貴金属の分散性を確保するため、比表面積の大きい耐熱性無機材料が適し、特に活性アルミナが好ましい。耐熱比表面積を高めるために希土類元素やジルコニア等を添加した活性アルミナを使用しても良い。活性アルミナの使用量は触媒１Ｌあたり、５０ｇより少ないと十分な貴金属の分散性が得られず、３００ｇより多く使用すると性能低下がみられる点から５０～３００ｇであることが好ましい。

【００１８】また、本発明の排気ガス浄化用触媒に用いるセリアは、ＮＯｘ酸化性能及び耐久性を高める点から、特にジルコニウム固溶型セリアが好ましい。ここで「固溶」とは、セリア中のセリウム原子の一部がジルコニウムと置換した状態のことをいい、この様な状態の酸化物は複合酸化物とも称される。該ジルコニウム固溶型セリアは、その成分の一部若しくは全部が複合化していることが好ましい。

【００１９】当該セリアの量は触媒１Ｌあたり１０～１００ｇであることが好ましい。１０ｇ未満だと三元性能もしくはＮＯｘ酸化能が十分に得られず、逆に１００ｇを超えても有為な増量効果は得られない。またジルコニウム固溶型セリアのジルコニウムとセリウムの比率は特に限定されないが、ジルコニウムのモル％が５～５０％であることが好ましい。ジルコニウムのモル％が前記範囲以外となると、ＮＯｘ吸収作用に必要なＮＯｘ酸化反応、あるいは耐熱性が低下することとなる。

【００２０】前記貴金属の一部もしくは全部がセリアに担持される構造により、ＮＯｘ吸収に必要なＮＯｘ酸化反応が更に高まり、優れたＮＯｘ吸収作用を得る。

【００２１】また、本発明の排気ガス浄化用触媒に用いるカリウム及びバリウムの含有量は、金属酸化物重量に換算して、触媒１Ｌあたり各々カリウムが０．１～２０ｇ、バリウムが０．１～１００ｇであることが好ましい。これより少ない量だとＮＯｘ吸収能が十分に得られず、またこれより多い量を加えても有為な増量効果は得られない。

【００２２】特に、請求項２記載の排気ガス浄化用触媒は、請求項１記載の触媒層Ａと、貴金属触媒層Ｂとを組み合わせて成るが、前記Ａ層及びＢ層の配置は、上層にＡ層下層にＢ層が位置しても、またこの逆であっても、いずれの場合においても層分離の効果が認められることから特に限定されない。

【００２３】前記貴金属触媒層Ｂ中の貴金属には、白金、ロジウム及びパラジウムから成る群より選ばれる少なくとも１種の貴金属が含まれる。またその貴金属の含有量は、ＮＯｘ吸収能とストイキ時の三元触媒性能が十分に得られれば特に限定されないが、０．１ｇより少ないと十分な三元性能が得られず、１０ｇより多く使用しても有意な性能向上はみられない点から触媒１Ｌあたり０．１～１０ｇが好ましい。また当該触媒層Ｂ中にはカ

リウムを含有してはならず、これは貴金属のＨＣ及びＣＯに対する酸化性能を低下させず高く維持するためである。

【００２４】当該触媒層Ｂ中の貴金属を担持するための基材には貴金属の分散性、特に耐久後の貴金属の分散性を確保するため、比表面積の大きい耐熱性無機材料が適し、特に活性アルミナが好ましい。耐熱比表面積を高めるために希土類元素やジルコニア等を添加した活性アルミナを使用しても良い。活性アルミナの使用量は触媒１Ｌあたり、５０ｇより少ないと十分な貴金属の分散性が得られずに性能が低下し、３００ｇより多く用いても性能低下がみられる点から５０～３００ｇであることが好ましい。

【００２５】また、請求項３記載の発明において、排気ガス流に対して上流側に設けられたＣｕ担持ゼオライト触媒の含有量は、ＮＯｘ浄化作用を示す量であれば特に限定されないが、１００ｇより少ないと十分なＮＯｘ還元性能が得られず、３００ｇより多く使用しても有意な性能向上はみられない点から触媒担体１Ｌあたり１００～３００ｇが好ましい。触媒活性及び耐久性を向上させるために、例えばＣｏ，Ｃａ，Ｐ，Ｃｅ，Ｎｄ等を添加してもよい。ゼオライトとしては、Ｃｕイオン交換後の活性が高くかつ耐熱性に優れるものが好ましく使用され、例えば、ペンタル型ゼオライト、Ｙ型ゼオライト、モルデナイト、フェリエライト等がある。

【００２６】当該Ｃｕ担持ゼオライト触媒と、請求項１又は２記載の触媒の排気系への設置方法は、Ｃｕ担持ゼオライト触媒を排気ガス流に対して上流側に、また請求項１又は２記載の触媒を排気ガス流に対して下流側に設置することが重要であり、例えば１個の触媒コンバータ内に２種の触媒を装着して配置する方法や、前記２種の触媒を別々のコンバータに入れて設置する方法等の公知の方法を用いることができる。触媒の設置位置は特に限定されず、例えばマニホールド直下位置や床下位置等があげられる。この触媒系の前段、後段それぞれ１個ずつの触媒で浄化性能が十分でない場合には、さらに前段、後段の何れかあるいは両方を複数個としたり、多種触媒を追加しても良い。

【００２７】本発明で用いられる触媒担体としては、公知の触媒担体の中から適宜選択して使用することができ、例えば耐火性材料からなるモノリス構造を有するハニカム担体やメタル担体等が挙げられる。この触媒担体の形状は、特に制限されないが、通常はハニカム形状で使用することが好ましく、このハニカム材料としては、一般にセラミック等のコージェライト質のものが多く用いられるが、フェライト系ステンレス等の金属材料からなるハニカムを用いることも可能であり、更には触媒粉末そのものをハニカム形状に成形しても良い。触媒の形状をハニカム状とすることにより、触媒と排気ガスの触媒面積が大きくなり、圧力損失も抑えられるため自動車用等として用いる場合に極めて有利である。

【００２８】本発明の排気ガス浄化用触媒を製造するには、例えば担持する元素の化合物を予め用意し、これらの混合物を湿式にて粉砕した水溶性スラリーをモノリス担体にコートし、乾燥した後焼成して得る方法、また、担持する元素のうちカリウム及びバリウム以外の成分をモノリス担体にコートし、乾燥した後焼成し、次いでカリウム及びバリウムの各成分の塩を含有する水溶性を含浸して得る方法がある。

【００２９】特に、請求項６記載の排気ガス浄化用触媒の製造方法は、耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成することを特徴とする。

【００３０】また、請求項７記載の排気ガス浄化用触媒の製造方法は、請求項６記載の排気ガス浄化用触媒を製造するにあたり、焼成温度を３００～６００℃とすることを特徴とする。

【００３１】触媒調製用原料化合物としては、硝酸塩、炭酸塩、アンモニウム塩、酢酸塩、ハロゲン化物、酸化物等を組み合わせて使用することができるが、特に水溶性の塩を使用することがＨＣ及びＮＯｘに対する触媒性能を向上させる観点から好ましい。調製法としては特殊な方法に限定されず、成分の著しい偏在を伴わない限り、公知の蒸発乾固法、沈殿法、含浸法等の種々の方法を用いることができる。

【００３２】特に、ジルコニウム固溶型セリアの製造方法は特に限定されないが、例えば、セリウム、ジルコニウムの塩を含む混合水溶液を乾燥した後、焼成して得る方法や、それぞれの塩の混合水溶液にアンモニウムや炭酸アンモニウムやクエン酸を添加して得た沈殿物を乾燥した後、焼成する方法がある。

【００３３】また、上記熱処理は、空気又は空気流通下で行ない、その焼成温度は、３００℃～６００℃が好ましく、３００℃未満だと全体が酸化物とならず、６００℃を超えると比表面積が低下し、望ましくない。

【００３４】

【作用】請求項１記載の排気ガス浄化用触媒は、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属と、セリアと、バリウム及びカリウムとを含有し、前記貴金属の一部又は全部がセリアに担持されて両者が共存することにより、ＮＯｘ吸収に必要なＮＯｘ酸化反応を向上させる。またバリウム及びカリウムとが、貴金属とセリアとの界面に接することで、バリウム及びカリウムとが本来有するＮＯｘ吸収能力が十分に発揮できることとなっている。これらの要因が重なって、ＮＯｘ吸収能を高め、かつ耐久後も触媒性能を低下

しにくくしている。

【００３５】特に、請求項２記載の排気ガス浄化用触媒は、上記貴金属と、セリアと、バリウム及びカリウムとを含有する触媒層Ａと上記貴金属担持触媒層Ｂとを組み合わせてなる二層構造とすることにより、ＮＯｘ吸収性能を得ながら、十分な三元触媒性能を得る。触媒層Ａ中の貴金属は、上記したように主にＮＯｘの吸収を促進させる作用を示すものである。一方触媒層Ｂ中の貴金属は、更にＨＣ及びＣＯの酸化を促進し、ＮＯｘの還元効率を向上させるものである。従って、触媒Ｂ層中にカリウムを含有すると、カリウムが前記貴金属のＨＣ及びＣＯ酸化性能を低下させるため、当該触媒層Ｂには、カリウムを含有してはならない。

【００３６】また特に、請求項３記載の排気ガス浄化用触媒に関して、従来は、例えばＣｕ担持ゼオライト触媒等のＮＯｘ浄化触媒と、Ｐｔ－ランタン触媒等のＮＯｘ吸収触媒はその特性上、前者は排気ガス中のＨＣ／ＮＯｘ比が小さいと浄化作用が十分に得られず、また後者ではリーンで定常走行を行うとＮＯｘ吸収量が飽和に達してやがて吸収作用が無くなるという問題があり、幅広い運転条件下でＮＯｘを浄化することができなかった。従って、請求項３記載の発明では、排気ガスを一旦Ｃｕ担持ゼオライト触媒に接触させることで、後段のＮＯｘ吸収触媒の吸収作用を高めている。その吸収作用は、例えばＣｕ担持ゼオライト触媒でＮＯｘ吸収に必要なＮＯｘの酸化が速やかに進行してＮＯｘ吸収材の働きを補助していることや、Ｃｕ担持ゼオライト触媒がＮＯｘ吸収に好都合なＨＣ、ＮＯｘ、$O_2$ 濃度に変換していることなどが考えられる。

【００３７】更に特に、請求項４記載の排気ガス浄化用触媒は、セリアがジルコニウム固溶型セリアであることより、純粋なセリアを用いた場合と比べ、ＮＯｘ酸化性能および耐久性が高まり、優れたＮＯｘ吸収作用、耐久性を得る。

【００３８】更に特に、請求項５記載の排気ガス浄化用触媒は、カリウム及びバリウムの含有量を各々上記したように限定することにより、ストイキ時の性能を確保しつつＮＯｘ吸収性能を得る。

【００３９】また、請求項６記載の排気ガス浄化用触媒の製造方法は、耐火性無機担体上に、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも一種の貴金属を担持したアルミナ粉末と、当該貴金属の一部若しくは全部を担持したセリア粉末とを触媒担体にコートした後、焼成し、次いでこれにカリウム及びバリウムの金属塩の混合水溶液を含浸した後、焼成する製法とすることで、貴金属とセリアとの界面にカリウム及びバリウムが接し、バリウムとカリウムとが本来有するＮＯｘ吸収能力を充分に発揮できることとなる。

【００４０】また、請求項７記載の排気ガス浄化用触媒の製造方法は、熱処理焼成温度を上記したように３００～６００℃と限定することにより、貴金属の分散性を損なうことなく、触媒中に貴金属の均一な分散性をもたらす。



【００４１】

【実施例】本発明を次の実施例及び比較例により説明する。

実施例１

活性アルミナ粉末に硝酸ロジウム（Ｒｈ）水溶液を含浸し、乾燥後４００℃で１時間焼成して、Ｒｈ担持活性アルミナ粉末（粉末Ａ）を得た。この粉末ＡのＲｈ濃度は２．０重量％であった。活性アルミナ粉末にジニトロジアミン白金（Ｐｔ）水溶液を含浸し、乾燥した後、４００℃で１時間焼成して、Ｐｔ担持活性アルミナ粉末（粉末Ｂ）を得た。この粉末ＢのＰｔ濃度は４．０重量％であった。上記Ｒｈ担持活性アルミナ粉末（粉末Ａ）１０８ｇ、Ｐｔ担持活性アルミナ粉末（粉末Ｂ）５３１ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末８１ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該コート層重量１００ｇ／Ｌ－担体の材料に、酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００４２】実施例２

カリウム及びバリウムの含有量を、各々酸化物に換算して１０ｇ／Ｌ、４０ｇ／Ｌとした以外は、実施例１と同様にして、排気ガス浄化用触媒を得た。

【００４３】実施例３

硝酸ジルコニウムと硝酸セリウムの混合水溶液にアンモニアを添加し、得られた沈殿物を濾過し、乾燥した後、４００℃で３時間焼成し、ジルコニウム固溶型セリア粉末（粉末Ｃ）を得た。当該ジルコニウム固溶型セリア粉末Ｃ中に含まれるジルコニウムの量は、金属モルに換算してＺｒ／Ｃｅ＝５／９５であった。このジルコニウム固溶型セリア粉末Ｃを、実施例１の活性セリア粉末のかわりに用いた以外は、実施例１と同様にして、排気ガス浄化用触媒を得た。

【００４４】実施例４

Ｚｒ／Ｃｅ＝４０／６０のジルコニウム固溶型セリア粉末（粉末Ｄ）を実施例３と同様の方法で得、このジルコニウム固溶型セリア粉末Ｄを実施例１の活性セリア粉末のかわりに用いた以外は、実施例１と同様にして、排気ガス浄化用触媒を得た。

【００４５】実施例５

活性セリア粉末にジニトロジアミン白金（Ｐｔ）水溶

液を含浸し、乾燥した後、４００℃で１時間焼成して、Ｐｔ担持活性セリア粉末（粉末Ｅ）を得た。この粉末ＥのＰｔ濃度は２．０重量％であった。実施例１で得られたＲｈ担持活性アルミナ粉末（粉末Ａ）１０８ｇとＰｔ担持活性アルミナ粉末（粉末Ｂ）３５１ｇ、上記Ｐｔ担持活性セリア粉末（粉末Ｅ）１８０ｇ、活性アルミナ粉末２６１ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該１００ｇ／Ｌ－担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００４６】実施例６

実施例５の活性セリア粉末のかわりに実施例３で得られたジルコニウム固溶型セリア粉末（粉末Ｃ）を用いた以外は、実施例５と同様にして、排気ガス浄化用触媒を得た。

【００４７】実施例７

実施例１で得られたＲｈ担持活性アルミナ粉末（粉末Ａ）７２ｇとＰｔ担持活性アルミナ粉末（粉末Ｂ）３４８ｇ、活性セリア粉末１２０ｇ、活性アルミナ粉末６０ｇ、酢酸カリウム１２４ｇ、酢酸バリウム４２８ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量７５ｇ／Ｌ－担体の下層触媒を得た。当該材料中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ，２０ｇ／Ｌであった。実施例１で得られたＲｈ担持活性アルミナ粉末（粉末Ａ）１０８ｇとＰｔ担持活性アルミナ粉末（粉末Ｂ）５４０ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末７２ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液を上記７５ｇ／Ｌ－担体に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成して上層触媒と下層触媒とを組み合わせてトータルでコート層重量１２５ｇ／Ｌ－担体の排気ガス浄化用触媒を得た。

【００４８】実施例８

実施例７における上層触媒を下層触媒として、下層触媒を上層触媒として、コート層の上下を逆にする以外は、実施例７と同様にして、排気ガス浄化用触媒を得た。

【００４９】比較例１

実施例１で得られたＲｈ担持活性アルミナ粉末（粉末Ａ）１０８ｇとＰｔ担持活性アルミナ粉末（粉末Ｂ）５３１ｇ、活性アルミナ粉末２６１ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該１００ｇ／Ｌ－担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００５０】比較例２

実施例１で得られたＲｈ担持活性アルミナ粉末（粉末Ａ）１０８ｇとＰｔ担持活性アルミナ粉末（粉末Ｂ）５３１ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末８１ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の排気ガス浄化用触媒を得た。

【００５１】実施例９

活性アルミナ粉末にジニトロジアンミンパラジウム水溶液を含浸し、乾燥した後、４００℃で１時間焼成して、Ｐｄ担持活性アルミナ粉末（粉末Ｆ）を得た。この粉末ＦのＰｄ濃度は４．０重量％であった。当該Ｐｄ担持活性アルミナ粉末（粉末Ｆ）６３０ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末９０ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該１００ｇ／Ｌ－担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００５２】実施例１０

カリウム及びバリウムの含有量を、各々酸化物に換算して１０ｇ／Ｌ、４０ｇ／Ｌとした以外は、実施例９と同様にして、排気ガス浄化用触媒を得た。

【００５３】実施例１１

実施例３で得られたジルコニウム固溶型セリア粉末（粉末Ｃ）を実施例９の活性セリア粉末のかわりに用いた以外は、実施例９と同様にして、排気ガス浄化用触媒を得

た。

【００５４】実施例１２

実施例４で得られたジルコニウム固溶型セリア粉末（粉末Ｄ）を実施例９の活性セリア粉末のかわりに用いた以外は、実施例９と同様にして、排気ガス浄化用触媒を得た。

【００５５】実施例１３

活性セリア粉末にジニトロジアンミンパラジウム水溶液を含浸し、乾燥した後、４００℃で１時間焼成して、Ｐｄ担持活性セリア粉末（粉末Ｇ）を得た。この粉末ＧのＰｄ濃度は４．０重量％であった。実施例９で得られたＰｄ担持活性アルミナ粉末（粉末Ｆ）４５０ｇ、上記Ｐｄ担持活性セリア粉末（粉末Ｇ）１８０ｇ、活性アルミナ粉末２７０ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該１００ｇ／Ｌ－担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して排気ガス浄化用触媒を得た。当該触媒１５中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００５６】実施例１４

実施例３で得られたジルコニウム固溶型セリア粉末（粉末Ｃ）を実施例１３の活性セリア粉末のかわりに用いた以外は、実施例１３と同様にして、排気ガス浄化用触媒を得た。

【００５７】実施例１５

実施例９で得られたＰｄ担持活性アルミナ粉末（粉末Ｆ）４２０ｇ、活性セリア粉末１２０ｇ、活性アルミナ粉末６０ｇ、酢酸カリウム１２４ｇ、酢酸バリウム４２８ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量７５ｇ／Ｌ－担体の下層触媒を得た。当該材料中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。実施例９で得られたＰｄ担持活性アルミナ粉末（粉末Ｆ）６３０ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末９０ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液を上記７５ｇ／Ｌ－担体に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成して上層触媒と下層触媒とを組み合わせてトータルで１２５ｇ／Ｌ－担体の排気ガス浄化用触媒を得た。

【００５８】実施例１６

実施例１５における上層触媒を下層触媒として、下層触媒を上層触媒として、コート層の上下を逆にする以外は、実施例１５と同様にして、排気ガス浄化用触媒を得た。

【００５９】比較例３

実施例９で得られたＰｄ担持活性アルミナ粉末（粉末Ｆ）６３０ｇ、活性アルミナ粉末２７０ｇ、水９００ｇを磁性ボールミルに加えて投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の材料を得た。当該１００ｇ／Ｌ－担体の材料に酢酸カリウムと酢酸バリウムの混合水溶液を含浸し、乾燥した後、４００℃で１時間焼成して、排気ガス浄化用触媒を得た。当該触媒中のカリウム及びバリウムの含有量は、各々酸化物に換算して５ｇ／Ｌ、２０ｇ／Ｌであった。

【００６０】比較例４

実施例９で得られたＰｄ担持活性アルミナ粉末（粉末Ｆ）６３０ｇ、活性セリア粉末１８０ｇ、活性アルミナ粉末９０ｇ、水９００ｇを加えて磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成してコート層重量１００ｇ／Ｌ－担体の排気ガス浄化用触媒を得た。

【００６１】実施例１７

０．２モル／Ｌの硝酸銅水溶液５．２ｋｇとゼオライト粉末２ｋｇとを混合して攪拌した後、濾過する作業を３回繰り返した後、乾燥、焼成し、Ｃｕ担持ゼオライト粉末（粉末Ｈ）を得た。この粉末ＨのＣｕ濃度は５％であった。このＣｕ担持ゼオライト粉末（粉末Ｈ）８１０ｇ、シリカゾル（固形分２０％）４５０ｇ、水５４０ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。このスラリー液をコーディエライト質モノリス担体（１．３Ｌ，４００セル）に付着させ、空気流にてセル内の余剰のスラリーを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成して、コート層重量３００ｇ／Ｌ－担体のＣｕ担持ゼオライト触媒を得た。このＣｕ担持ゼオライト触媒を排気流れの上流側に、また実施例１で得られた触媒を下流側に配置した。

【００６２】実施例１８

実施例１７で得られたＣｕ担持ゼオライト触媒を排気流れの上流側に、また実施例２で得られた触媒を下流側に配置した。

【００６３】実施例１９

実施例１７で得られたＣｕ担持ゼオライト触媒を排気流

れの上流側に、また実施例3で得られた触媒を下流側に配置した。

【0064】実施例20

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例4で得られた触媒を下流側に配置した。

【0065】実施例21

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例5で得られた触媒を下流側に配置した。

【0066】実施例22

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例6で得られた触媒を下流側に配置した。

【0067】実施例23

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例7で得られた触媒を下流側に配置した。

【0068】実施例24

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例8で得られた触媒を下流側に配置した。

【0069】実施例25

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例9で得られた触媒を下流側に配置した。

【0070】実施例26

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例10で得られた触媒を下流側に配置した。

【0071】実施例27

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例11で得られた触媒を下流側に配置した。

【0072】実施例28

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例12で得られた触媒を下流側に配置した。

【0073】実施例29

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例13で得られた触媒を下流側に配置した。

【0074】実施例30

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例14で得られた触媒を下流側に配置した。

【0075】実施例31

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例15で得られた触媒を下流側に配置した。

【0076】実施例32

実施例17で得られたCu担持ゼオライト触媒を排気流れの上流側に、また実施例16で得られた触媒を下流側に配置した。

【0077】上記実施例1～32及び比較例1～4の触媒組成を次の表1及び2に示す。

【表1】

| | 貴金属（g/L） | | | 添加材（酸化物g/L） | | |
|---|---|---|---|---|---|---|
| | Pt | Rh | Pd | Ce | K | Ba |
| 実施例1<br>実施例17 | 1.18 | 0.24 | － | 20.0 | 5.0 | 20.0 |
| 実施例2<br>実施例18 | 1.18 | 0.24 | － | 20.0 | 10.0 | 40.0 |
| 実施例3<br>実施例19 | 1.18 | 0.24 | － | 20.0(*1) | 5.0 | 20.0 |
| 実施例4<br>実施例20 | 1.18 | 0.24 | － | 20.0(*2) | 5.0 | 20.0 |
| 実施例5<br>実施例21 | 1.18 | 0.24 | － | 20.0 | 5.0 | 20.0 |
| 実施例6<br>実施例22 | 1.18 | 0.24 | － | 20.0 | 5.0 | 20.0 |
| 実施例7<br>実施例23 | 1.18 | 0.24 | － | 20.0 | 5.0 | 20.0 |
| 実施例8<br>実施例24 | 1.18 | 0.24 | － | 20.0 | 5.0 | 20.0 |
| 実施例9<br>実施例25 | － | － | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例10<br>実施例26 | － | － | 2.83 | 20.0 | 10.0 | 40.0 |
| 実施例11<br>実施例27 | － | － | 2.83 | 20.0(*1) | 5.0 | 20.0 |
| 実施例12<br>実施例28 | － | － | 2.83 | 20.0(*2) | 5.0 | 20.0 |
| 実施例13<br>実施例29 | － | － | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例14<br>実施例30 | － | － | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例15<br>実施例31 | － | － | 2.83 | 20.0 | 5.0 | 20.0 |
| 実施例16<br>実施例32 | － | － | 2.83 | 20.0 | 5.0 | 20.0 |

(*1)：Zr／Ceモル比＝5／95
(*2)：Zr／Ceモル比＝40／60

【表2】

| | 貴金属（g/L） | | | 添加材（g/L） | | |
|---|---|---|---|---|---|---|
| | Pt | Rh | Pd | Ce | K | Ba |
| 比較例1 | 1.18 | 0.24 | － | － | 5.0 | 20.0 |
| 比較例2 | 1.18 | 0.24 | － | 20.0 | － | － |
| 比較例3 | － | － | 2.83 | － | 10.0 | 10.0 |
| 比較例4 | － | － | 2.83 | 20.0 | － | － |

【0078】試験例1

前記実施例1～32及び比較例1～4の触媒及び触媒シ

ステムについて、以下の条件で初期及び耐久後の触媒活性評価を行った。活性評価には、自動車の排気ガスを模したモデルガスを用いる自動評価装置を用いた。

【００７９】耐久条件

エンジン４４００ｃｃの排気系に触媒を装着し、６００℃で、５０時間運転して耐久を行った。

【００８０】評価条件

触媒活性評価は、排気量２０００ｃｃのエンジンの排気系に各触媒を装着し、Ａ／Ｆ＝１４．６（ストイキ状＊態）で３０秒間、その後Ａ／Ｆ＝２２（リーン雰囲気）で３０秒間の運転を１サイクル行ない、各々平均転化率を測定し、このＡ／Ｆ＝１４．６（ストイキ状態）の場合の平均転化率とＡ／Ｆ＝２２（リーン雰囲気）の場合の平均転化率とを平均してトータル転化率とした。この評価を初期及び耐久後に各々行ない、触媒活性評価値を以下の式により決定した。

【数１】

$$\text{NOx転化率(\%)} = \frac{\text{〔触媒層入口NOx濃度〕} - \text{〔触媒層出口NOx濃度〕}}{\text{〔触媒層入口NOx濃度〕}} \times 100$$

（ＨＣ．ＣＯも同様）

【００８１】トータル転化率として得られた触媒活性評価結果を表３～５に示す。比較例に比べて実施例は、触媒活性が高く、後述する本発明の効果を確認することができた。

【表３】

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | ＨＣ | ＣＯ | ＮＯｘ | ＨＣ | ＣＯ | ＮＯｘ |
| 実施例１ | 91 | 100 | 90 | 92 | 97 | 62 |
| 実施例２ | 88 | 99 | 93 | 91 | 97 | 65 |
| 実施例３ | 93 | 100 | 92 | 95 | 99 | 67 |
| 実施例４ | 93 | 100 | 92 | 96 | 99 | 66 |
| 実施例５ | 92 | 100 | 92 | 93 | 97 | 64 |
| 実施例６ | 96 | 100 | 95 | 95 | 99 | 68 |
| 実施例７ | 92 | 100 | 91 | 93 | 98 | 63 |
| 実施例８ | 91 | 100 | 91 | 93 | 98 | 63 |
| 比較例１ | 88 | 100 | 87 | 89 | 95 | 59 |
| 比較例２ | 90 | 100 | 89 | 90 | 96 | 50 |

【表４】

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | ＨＣ | ＣＯ | ＮＯｘ | ＨＣ | ＣＯ | ＮＯｘ |
| 実施例９ | 95 | 100 | 93 | 96 | 99 | 65 |
| 実施例10 | 89 | 99 | 93 | 94 | 98 | 67 |
| 実施例11 | 93 | 100 | 95 | 95 | 99 | 68 |
| 実施例12 | 95 | 100 | 96 | 96 | 99 | 68 |
| 実施例13 | 95 | 100 | 96 | 95 | 97 | 65 |
| 実施例14 | 97 | 100 | 96 | 95 | 99 | 70 |
| 実施例15 | 94 | 100 | 93 | 94 | 98 | 65 |
| 実施例16 | 94 | 100 | 93 | 95 | 98 | 63 |
| 比較例３ | 89 | 100 | 89 | 89 | 95 | 56 |
| 比較例４ | 90 | 100 | 89 | 90 | 96 | 51 |

【表５】

| | 初期転化率 % | | | 耐久後転化率 % | | |
|---|---|---|---|---|---|---|
| | ＨＣ | ＣＯ | ＮＯｘ | ＨＣ | ＣＯ | ＮＯｘ |
| 実施例17 | 92 | 100 | 98 | 92 | 98 | 77 |
| 実施例18 | 90 | 100 | 98 | 91 | 98 | 79 |
| 実施例19 | 93 | 100 | 96 | 95 | 99 | 78 |
| 実施例20 | 93 | 100 | 96 | 96 | 99 | 80 |
| 実施例21 | 92 | 100 | 97 | 93 | 97 | 82 |
| 実施例22 | 96 | 100 | 96 | 95 | 99 | 83 |
| 実施例23 | 92 | 100 | 98 | 93 | 98 | 79 |
| 実施例24 | 91 | 100 | 98 | 94 | 98 | 79 |
| 実施例25 | 96 | 100 | 97 | 90 | 95 | 79 |
| 実施例26 | 94 | 100 | 95 | 93 | 96 | 80 |
| 実施例27 | 95 | 100 | 96 | 96 | 99 | 80 |
| 実施例28 | 95 | 99 | 96 | 95 | 98 | 80 |
| 実施例29 | 96 | 100 | 98 | 96 | 99 | 83 |
| 実施例30 | 98 | 100 | 96 | 95 | 99 | 86 |
| 実施例31 | 95 | 100 | 96 | 95 | 98 | 80 |
| 実施例32 | 95 | 100 | 97 | 95 | 98 | 80 |

【００８２】
【発明の効果】請求項１記載の排気ガス浄化用触媒は、貴金属と、セリアと、バリウム及びカリウムを含有し、貴金属の一部又は全部がセリアに担持されていることにより、従来の触媒では十分な活性が得られないリーン雰囲気下におけるＮＯｘ浄化性能を、ＮＯｘ吸収に必要なＮＯｘ酸化反応を向上させることにより高めることができ、かつ耐久後においても三元触媒としての機能を十分に発現することができる。

【００８３】請求項２記載の排気ガス浄化用触媒は、更に貴金属担持層と、請求項１記載の触媒層とを、任意に上下に組み合わせることにより、前記効果に加えて更にＨＣ及びＣＯ活性を向上させることができる。

【００８４】請求項３記載の排気ガス浄化用触媒は、排気気流に対して上流側に銅担持ゼオライト含有触媒を、下流側に上記請求項１又は２記載の触媒を配置することにより、上記効果に加えて、更にＮＯｘ吸収作用を高めることができる。

【００８５】請求項４記載の排気ガス浄化用触媒は、更にセリアをジルコニウム固溶型セリアとすることにより、上記効果に加えて、ＮＯｘ酸化性能及び耐久性を更に高めることができる。

【００８６】請求項５記載の排気ガス浄化用触媒は、更にカリウム及びバリウムの含有量を特定することにより、上記効果に加えて、ストイキ時の性能も確保されることとなる。

【００８７】請求項６記載の排気ガス浄化用触媒の製造方法は、上記説明した工程を経ることにより、貴金属とセリアとの界面にカリウム及びバリウムが十分に接することができ、これによりＮＯｘ吸収能力を充分に発揮できる請求項１記載の排気ガス浄化用触媒を簡便に製造することができる。

【００８８】請求項７記載の排気ガス浄化用触媒の製造方法は、更に熱処理焼成温度を限定することにより、上記効果に加えて、排気ガス浄化用触媒中への貴金属の分散を、更に均一にすることができる。

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